Supplementary Information

Silver paste engineered interphase enables highly reversible and

dendrite-free Zn metal anodes

Yi Ding, Min Guo*, Song Lu, Tiancun Liu, Qi Shen, Jiadi Ying, Yeqing Wang, Zhixin Yu*

EXPERIMENTAL SECTION

Preparation of Zn@SP anode

High-purity Zn foil (thickness: 0.04 mm, purity: 99.99%) was purchased from Canrd New Energy technology. The Zn foil was thoroughly cleaned with anhydrous ethanol to remove surface impurities and then cut into circular discs with a diameter of 10 mm. Self-spraying conductive silver paste was obtained from Shenzhen Jingzhe technology Co., Ltd.

Prior to spraying, the aerosol should be vigorously shaken for 30 seconds in all directions (up, down, left, and right) to ensure the uniformity of the slurry. The coating was applied via horizontal spraying motions, maintaining a perpendicular orientation to the substrate surface. The nozzle was positioned 5 to 10 cm from the target surface. The spraying system featured a nozzle aperture of 0.1 mm diameter, with an operational pressure ranging 0.3 to 0.6 MPa and a spray fan angle of 40-80°. All coating procedures were conducted under strictly controlled environmental conditions, including a windless atmosphere, high cleanliness, and ambient temperature. After spraying, the treated Zn foil was allowed to dry naturally at room temperature for 30 min. The thickness of the coating layer was approximately 10 µm.

Materials characterization

X-ray diffraction (XRD, Empyrean) with CuK α radiation was employed to investigate the structure of samples in the 2 θ range of 10 – 70°. The surface electronic states were analyzed by X-ray photoelectron spectroscopy (XPS, K-Alpha). The morphology of electrode was recorded using scanning electron microscope (SEM, JSM-6360LV). Energy dispersion spectroscopy (EDS) was used to analyses the element distribution. The water contact angle of electrode is measured by a contact angle apparatus (JC2000D1).

Electrochemical measurement

All batteries were assembled with CR2032-type cells in the air. The component of

electrolyte was 2.0 M ZnSO₄ or trifluoromethanesulfonate (Zn(OTf)₂) in water. Glassfiber (Whatman, GF/D) was used as separator. To assemble full-cell, V2O5 cathode (active material), super P (conductive carbon), and poly (vinyl difluoride) (PVDF) (binder) were mixed in N-methyl-pyrrolidone (NMP) with a weight ratio of 7:2:1, and coated at stainless steel foil. The foil was dried at 90 °C under vacuum for 12 h. The obtained foil was cut into wafers with a diameter of 10 mm. The weight loading of active material is about 1-2 mg cm⁻². The ammonium metavanadate (NVO, Canrd Co., Ltd.) cathode sheet was prepared using the same method. Na-doped V₂O₅ on stainlesssteel mesh is purchased from Canrd Co., Ltd. Neware battery test system was used to obtain galvanostatic charge/discharge performance at various current densities. The voltage range of electrochemical test of full cells is 0.2-1.6 V. The electrochemical kinetics (100 kHz to 0.01 Hz, amplitude is 5 mV) and CV curve (scan rate is 0.1 mV s⁻¹) of the newly assembled cells were monitored on an electrochemical working station (VSP, Biologic). The impedance of Zn@SP||Zn@SP symmetric cells was measured after galvanostatic charge/discharge at a current density of 1 mA cm⁻² and 1 mAh cm⁻² for 25, 50, 100 and 150 cycles, analyzing the impedance characteristics of symmetric cells at different cycling stages.

The data from the impedance measurement were fitted with EC-lab software. Linear sweep voltammetry (LSV) was tested with three-electrodes system, using zinc foil as working electrode, platinum electrode as opposite electrode, Ag/AgCl₃ electrode as reference electrode at a scan rate of 10 mV s⁻¹. Fresh cells were assembled for chronoamperometry (CA) test at a potential of -150 mV.

Computational method

Density functional theory (DFT) calculations were performed in planewave basis set as implemented in the Vienna Ab Initio Simulation Package (VASP) ^{1,2}. The exchange– correlation interactions were determined by the Perdew–Burke–Ernzerhof functional (PBE) within the generalized gradient approximation (GGA) ³. The plane-wave basis was set with a cutoff energy of 450 eV. The convergence criteria for the energy and force were set to 1×10^{-5} eV and 0.02 eV/Å, respectively. A Monkhorst–Pack k-point mesh of $8 \times 8 \times 1$ were used for the structure optimization. The empirical correction in Grimme's method (DFT + D3) was used to describe the van der Waals interactions. The binding energy (E_{abs}) of Zn on different supports were calculated based on the equation below:

$$E_{ads} = E_{Zn-Sub} - E_{Zn} - E_{sub}$$

where the E_{Zn-Sub} , E_{Zn} , E_{sub} are the total energies of Zn-adsorbed substrate, single Zn atom and clean substrate.

The Gibbs free energy changes (ΔG) of *H on Zn, Cu and Ag surface were calculated by the following equation:

$$\Delta G = \Delta E + \Delta Z P E - T \Delta S$$

where $\triangle E$, $\triangle ZPE$ and $\triangle S$ are the differences in the total energy calculated from DFT calculations, variation of zero-point energy and entropy before and after reactions. T is the temperature at 298.15 K.



Fig. S1 SEM images and EDS mappings of (a-b) bare Zn foil and (c-f) Zn@SP anode.



Fig. S2 Digital photos of Zn@SP anode after immersed at 2M ZnSO₄ for 0, 2 and 7

days.



Fig. S3 X-ray Photoelectron Spectroscopy (XPS) spectra of Zn@SP anode before cycling.



Fig. S4 X-ray diffraction of Zn@SP anode after cycling at 1 mA cm⁻² and 1 mAh cm^{-2} for 10 and 100 cycles.



Fig. S5 XRD patterns and the corresponding enlargement of Zn@SP after 5 and 10 cycles at 1 mA cm⁻² and 1 mAh cm⁻².



Fig. S6 SEM images of Zn@SP anode after 0, 1 and 2 cycles at 1 mA cm⁻² and 1

 $mAh cm^{-2}$.



Fig. S7 The comparison of X-ray diffraction for bare Zn and Zn@SP electrodes after repeated cycles at 1 mA cm⁻² and 1 mAh cm⁻².



Fig. S8 The voltage-time profiles of Zn $\|Cu@SP\|$ and Zn $@SP\|$ Cu half-cells at 1 mA cm⁻² and 1 mAh cm⁻².



Fig. S9 Schematic illustration of the Zn dissolution process of Zn@SP.



Fig. S10 Voltage-time curves of (a) bare Zn; (b) Cu-Zn; (c) Ag-Zn electrodes at 1 mA cm⁻² and 1 mAh cm⁻².



Fig. S11 Equivalent circuit model for resistance fitting.



Fig. S12 Voltage-time curves of (a) Zn@SP and (b) bare Zn symmetric cells at 1 mA cm⁻² (1 mAh cm⁻²). (c) Nyquist plots of bare Zn symmetric cell after the 135th cycle.



Fig. S13 LSV curves of Ag-Zn, Cu-Zn at 10 mV s⁻¹.



Fig. S14 Cycling performance of full-cells with Zn(OTf)₂ electrolyte.



Fig. S15 Rate performances of full cells with Na-doped $\mathrm{V_2O_5}$ cathode.



Fig. S16 Rate performances of full cells with ammonium metavanadate cathode.

Materials	Current density (mA cm ⁻²)	Capacity (mAh cm ⁻²)	Cycle life (h)	Overpotential (mV)	Refs
Cu–Zn	0.5	0.5	1300	~45	4
Zn@Ag	1	1	500	~50	5
CuO@Zn	1	1	900	20	6
Zn@Sb	1	1	800	~26	7
NVP@Zn	0.5	0.25	500	~32	8
NZSP-Zn	0.5	0.5	1360	~19	9
BTO@Zn	1	1	2000	~20	10
Zn@CaF2	1	1	750	~40	11
ZnSe@Zn	1	1	1530	41	12
Zn@AC	1	1	500	31	13
NFSS@Zn	1	1	1500	25	14
3D MXene array@Zn	1	1	1500	45	15
Zn@UO-24	1	1	1600	~20	16
Zn@LDH	0.5	0.5	1500	31.6	17
ZnOHF NWs@Zn	1	1	700	27.6	18
MA-BTA@Zn	1	1	1800	~40	19
MB@Zn	0.2	0.1	1600	28.1	20
Zn-Li-Mn	1	1	1200	30	21
GI@Zn	1	0.1	1200	44	22
HP@Zn	2	1	1300	~20	23
	0.5	0.5	3500	~25	TL
Zn@SP	1	1	2200	~40	1 nis work
	3	3	1500	~43	

 Table S1 Comparison of electrochemical performance of Zn@SP||Zn@SP symmetric

 cells and various reported materials for the modification of zinc anode.

References

- 1 G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169-11186.
- 2 G. Kresse and J. Furthmüller, Comp. Mater. Sci., 1996, 6, 15-50.
- 3 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, 77, 3865-3868.

4 W. Huang, Y. Huang, X. Huang, F. Shao, W. Liu and F. Kang, *Small*, 2024, **20**, e2404294.

5 X. Zhou, B. Wen, Y. Cai, X. Chen, L. Li, Q. Zhao, S. L. Chou and F. Li, *Angew. Chem. Int. Ed.*, 2024, **63**, e202402342.

6 G.-Q. Liu, B. Fu, Z.-X. Liu, L.-Y. Li, S.-Q. Liang and G.-Z. Fang, *Rare Met.*, 2024, **43**, 5005-5016.

7 L. Hong, L. Y. Wang, Y. Wang, X. Wu, W. Huang, Y. Zhou, K. X. Wang and J. S. Chen, *Adv. Sci.*, 2022, **9**, e2104866.

8 N. Guo, Z. Peng, W. Huo, Y. Li, S. Liu, L. Kang, X. Wu, L. Dai, L. Wang, S. C. Jun and Z. He, *Small*, 2023, **19**, e2303963.

9 X. Liu, Q. Lu, A. Yang and Y. Qian, Chinese. Chem. Lett., 2023, 34, 107703.

10 K. Wu, J. Yi, X. Liu, Y. Sun, J. Cui, Y. Xie, Y. Liu, Y. Xia and J. Zhang, *Nano Micro Lett.*, 2021, **13**, 79.

11 Y. Li, S. Yang, H. Du, Y. Liu, X. Wu, C. Yin, D. Wang, X. Wu, Z. He and X. Wu, *J. Mater. Chem. A*, 2022, **10**, 14399-14410.

12 X. Yang, C. Li, Z. Sun, S. Yang, Z. Shi, R. Huang, B. Liu, S. Li, Y. Wu, M. Wang, Y. Su, S. Dou and J. Sun, *Adv. Mater.*, 2021, **33**, e2105951.

13 L. Li, Y. Zhang, C. Du, X. Zhou, H. Xiong, G. Wang and X. Lu, J. Colloid Interface Sci., 2024, 657, 644-652.

14 J. Duan, J. Dong, R. Cao, H. Yang, K. Fang, Y. Liu, Z. Shen, F. Li, R. Liu, H. Li and C. Chen, *Adv. Sci.*, 2023, **10**, e2303343.

15 J. Ruan, D. Ma, K. Ouyang, S. Shen, M. Yang, Y. Wang, J. Zhao, H. Mi and P. Zhang, *Nano Micro Lett.*, 2023, **15**, 37.

16 Q. Gou, Z. Chen, H. Luo, J. Deng, B. Zhang, N. Xu, J. Cui, Y. Zheng, M. Li and J. Li, *Small*, 2024, **20**, e2305902.

17 Y. Yang, C. Liu, Z. Lv, H. Yang, X. Cheng, S. Zhang, M. Ye, Y. Zhang, L. Chen, J. Zhao and C. C. Li, *Energy Storage Mater.*, 2021, **41**, 230-239.

18 Z. Pan, Q. Cao, W. Gong, J. Yang, Y. Gao, Y. Gao, J. Pu, J. Sun, X. J. Loh, Z. Liu, C. Guan and J. Wang, *Energy Storage Mater.*, 2022, **50**, 435-443.

19 J. Ding, J. He, L. Chen, Y. Sun, Y. Xu, L. P. Lv and Y. Wang, *Angew. Chem. Int. Ed.*, 2025, **64**, e202416271.

20 T. Huang, K. Xu, N. Jia, L. Yang, H. Liu, J. Zhu and Q. Yan, *Adv. Mater.*, 2023, **35**, e2205206.

21 Y. Zhang, X. Yang, Y. Hu, K. Hu, X. Lin, X. Liu, K. M. Reddy, G. Xie and H. J. Qiu, *Small*, 2022, **18**, e2200787.

22 C. Liu, Z. Luo, W. Deng, W. Wei, L. Chen, A. Pan, J. Ma, C. Wang, L. Zhu, L. Xie, X.-Y. Cao, J. Hu, G. Zou, H. Hou and X. Ji, *ACS Energy Lett.*, 2021, **6**, 675-683.

23 Y. Zou, Y. Su, C. Qiao, W. Li, Z. Xue, X. Yang, M. Lu, W. Guo and J. Sun, *Adv. Energy Mater.*, 2023, **13**, 2300932.